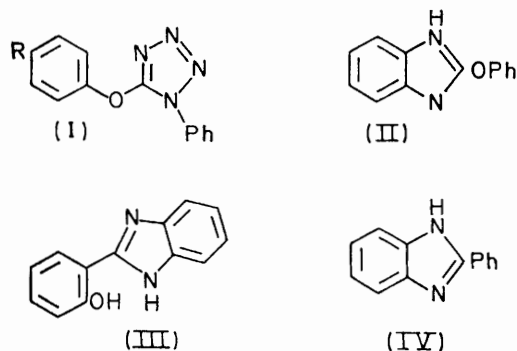


Photolysis of 5-Aryloxy-1-phenyl-1*H*-tetrazoles, and Photo-Fries Rearrangement of 2-Aryloxybenzimidazole

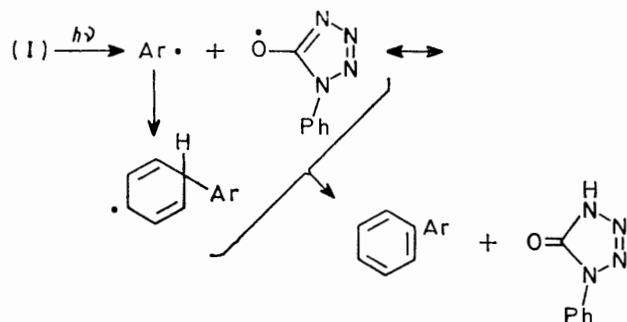
By Peter D. Hobbs and Philip D. Magnus,* Chemistry Department, Imperial College, London SW7

Photolysis of 5-phenoxy-1-phenyl-1*H*-tetrazole (I; R = H) in benzene gave 2-phenoxybenzimidazole (II), 2-(*o*-hydroxyphenyl)benzimidazole (III), 2-phenylbenzimidazole (IV), and biphenyl; the product (III) is derived from a photo-Fries rearrangement of (II).

WHEREAS the thermal chemistry of tetrazoles has received much attention,¹ little is known about their photochemical transformations.² Recently it was reported that photolysis of 5-phenoxy-1-phenyl-1*H*-tetrazole (I; R = H) in acetonitrile gave 2-phenoxy-



benzimidazole (II) (25%),³ 5-Aryloxy-1-phenyl-1*H*-tetrazoles (I) were of interest to us since hydrogenation



SCHEME 1

cleaves the aryl-oxygen bond, giving the deoxygenated aromatic hydrocarbon.⁴ If homolytic cleavage of the aryl-oxygen bond could be engendered photochemically, the resulting aryl radicals could be trapped by solvent (benzene) to give biphenyls. Such a process (Scheme 1)

† Compound (III) supplied by Dr. D. Goodgame of this Department.

¹ (a) R. Huisgen, M. Seidel, J. Sauer, J. W. McFarland, and G. Wallbillich, *J. Org. Chem.*, 1959, **24**, 892; (b) J. Sauer and K. K. Mayer, *Tetrahedron Letters*, 1968, 325; (c) J. S. Clovis, A. Eckell, R. Huisgen, and R. Sustmann, *Ber.*, 1967, **100**, 60.

² (a) S. T. Reid, *Adv. Heterocyclic Chem.*, 1970, **11**, 1; (b) R. M. Moriarity and J. M. Kliegman, *J. Amer. Chem. Soc.*, 1967, **89**, 5959.

³ F. L. Bach, J. Karliner, and G. E. Van Lear, *Chem. Comm.*, 1969, 1110.

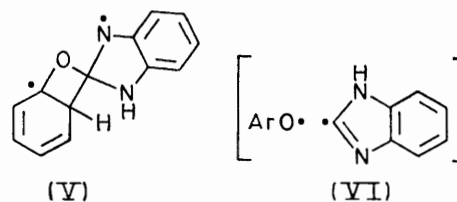
⁴ W. J. Musliner and J. W. Gates, jun., *J. Amer. Chem. Soc.*, 1966, **88**, 4271.

would provide a source of aryl radicals from commonly occurring phenols, and represent a synthetic method of converting an aryl-oxygen bond into an aryl-carbon bond.

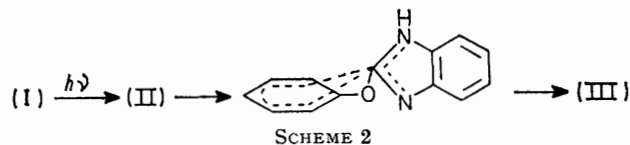
Irradiation of compound (I; R = H) in benzene gave a mixture from which four products were isolated: 2-phenoxybenzimidazole⁵ (II) (36%), as previously observed,³ biphenyl (10–15%), 2-(*o*-hydroxyphenyl)benzimidazole⁶ (III) (22%), and 2-phenylbenzimidazole⁷ (IV) (25%), all identified by comparison with authentic samples.†

Irradiation of compound (I; R = H) in cyclohexane gave a mixture from which compounds (II) and (III) were the only products isolated. Oxygen did not affect the product distribution. Blank experiments, in which benzene was irradiated alone, gave biphenyl (<3%).

Since the product (III) appears to arise from a photo-Fries-type rearrangement of 2-phenoxybenzimidazole (II) the photolysis of (II) was examined. Irradiation in benzene gave compounds (III) (50%) and (IV) (25%). The photo-Fries rearrangement⁸ has not been previously



observed for a heterocyclic system. The mechanism put forward by Anderson and Reese⁹ would lead to the



intermediate (V). The Woodward-Hoffmann formulation of the photo-Fries rearrangement as a [1,3] sigmatropic change (Scheme 2) appears to be a more

⁵ T. A. M. Sasajuna and Y. Watanabe, *J. Pharm. Soc. Japan*, 1965, **85**, 962.

⁶ J. L. Walter and L. Freiser, *Analyt. Chem.*, 1953, **25**, 127.

⁷ L. Hunter and J. A. Marriot, *J. Chem. Soc.*, 1941, 777.

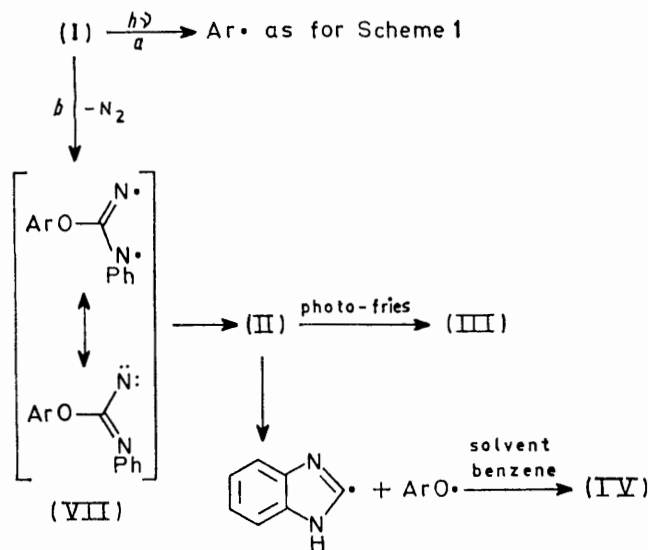
⁸ V. I. Stenberg, in 'Organic Photochemistry,' ed. O. L. Chapman, Edward Arnold, London, 1967, p. 127; (b) D. Bellus, *Adv. Photochem.*, 1917, **8**, 109.

⁹ J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1963, 1781.

acceptable mechanism.¹⁰ The 'cage-radical' postulate¹¹ (VI) has been used as a mechanistic interpretation of the photo-Fries rearrangement. Although escape from the cage adequately explains the formation of compound (IV) it is not a corollary that (III) should also be produced *via* the 'cage-radical' (VI). We were unable to isolate any products of *para*-Fries-type rearrangements, and if phenols were present they must have constituted less than 5% of the total reaction mixture.

Irradiation of compound (I; R = OMe) in benzene gave 4-methoxybiphenyl (11%) and 2-phenylbenzimidazole (IV) (21%). The other products were analogous (t.l.c. properties) to (II) and (III) but were not examined further. Similarly irradiation of compound (I; R = Ph) in benzene gave *p*-terphenyl (8%).

The photochemistry of 5-aryloxy-1-phenyl-1H-tetrazoles appears to involve at least two competing pathways (Scheme 3), and the product (II) from path *b* apparently undergoes two distinct photochemical processes. Path *a* involves aryl-oxygen bond cleavage and formation of biphenyls. Path *b* involves extrusion of nitrogen to give the diradical \leftrightarrow nitrene intermediate (VII) which cyclises to (II). The product (II) undergoes photo-Fries rearrangement to (III), and in



competition fragments to the benzimidazolyl radical and phenoxy-radicals. The benzimidazolyl radical is trapped by solvent (benzene) as 2-phenylimidazole (IV). A more detailed analysis of the products [several minor ones (*ca.* 10%) are formed] might reveal the fate of the phenoxy-radicals.

Since the biphenyls are formed in similar yields it would appear that the extrusion of nitrogen (this part of

the molecule is chromophorically the same in all substrates) drastically limits the amount of aryl-oxygen bond cleavage observed.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were measured for Nujol mulls and solutions in chloroform unless otherwise stated. N.m.r. spectra were recorded with a Varian A60 instrument for solutions in [²H]chloroform with tetramethylsilane as internal standard.

All solvents were purified prior to use by standard techniques. Light petroleum refers to the fraction b.p. 40–60 °C.

All photolyses were carried out by use of a Hanovia immersion medium-pressure light source, in quartz apparatus with reagents under a stream of argon.

Photolysis of 5-Phenoxy-1-phenyl-1H-tetrazole (I; R = H).—The tetrazole **4** (I; R = H) [λ_{max} (EtOH) 228 nm (ϵ 12,190)] (400 mg) in benzene (1 l) was irradiated for 46 h. The mixture was evaporated and the residue chromatographed on preparative silica gel plates (Merck GF₂₅₄), with benzene-ethyl acetate (17:3) as eluant, to give 2-phenoxybenzimidazole (II) (36%), m.p. 229–230° (lit.,⁵ 229–230°), λ_{max} (EtOH) 281, 274.5, and 237sh nm (ϵ 7810, 8280, and 8650); 2-(*o*-hydroxyphenyl)benzimidazole (III) (22%), m.p. 242–244° (lit.,⁶ 242–244°), λ_{max} (EtOH) 331.5, 317.5, 292, 286, 273.5, 263sh, 248, 240, and 234 nm (ϵ 19,400, 20,900, 13,600, 11,100, 8600, 6300, 6900, 11,100, and 11,500), ν_{max} (Nujol) 3300, 1640, 1600, and 1260 cm⁻¹; 2-phenylbenzimidazole (IV) (25%), m.p. 291–293° (lit.,⁷ 291–293°), λ_{max} (EtOH) 317, 303.5, 296.5, and 241.5 nm (ϵ 13,100, 23,100, 20,900, and 11,800), ν_{max} (Nujol) 2800 and 760 cm⁻¹; and biphenyl (10–15%), all identical with authentic samples.

The reaction was unaffected by oxygen. Irradiating benzene (1 l) under identical conditions gave biphenyl (*ca.* 3%).

Photolysis of 5-Phenoxy-1-phenyl-1H-tetrazole (I; R = H).—The tetrazole (I; R = H) (400 mg) in cyclohexane (1 l) was irradiated for 46 h. Work-up as before gave 2-phenoxybenzimidazole (II) (62.7 mg), m.p. 229–230°, and 2-(*o*-hydroxyphenyl)benzimidazole (III) (50.5 mg), m.p. 242–244°. No biphenyl was formed.

Photolysis of 2-Phenoxybenzimidazole (II).—2-Phenoxybenzimidazole (II) (30 mg) in benzene (1 l) was irradiated for 22 h. Work-up as before gave 2-(*o*-hydroxyphenyl)benzimidazole (III) (50%) and 2-phenylbenzimidazole (IV) (25%).

*Photolysis of 5-(*p*-Methoxyphenoxy)-1-phenyl-1H-tetrazole* (I; R = OMe).—The tetrazole (I; R = OMe) (400 mg) in benzene (1 l) was irradiated for 48 h. Work-up as before gave 4-methoxybiphenyl (11%) and 2-phenylbenzimidazole (IV) (21%), identical with authentic samples (m.p. and mixed m.p.).

Photolysis of 5-(Biphenyl-4-yloxy)-1-phenyl-1H-tetrazole (I; R = Ph).—The tetrazole (400 mg) in benzene (1 l) was irradiated for 60 h. Work-up as before gave *p*-terphenyl (8%), identical with an authentic sample (m.p. and mixed m.p.).

[2/2189 Received, 18th September, 1972]

¹⁰ M. R. Sandner, E. Hedaya, and D. J. Trecker, *J. Amer. Chem. Soc.*, 1968, **90**, 7249.

¹¹ (a) H. Kobsa, *J. Org. Chem.*, 1962, **27**, 2293; (b) R. A. Finnegan and J. J. Mattice, *Tetrahedron*, 1965, **21**, 1015.